

## JOINT INVENTORS

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## APPLICATION FOR UNITED STATES LETTERS PATENT

## S P E C I F I C A T I O N

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TO ALL WHOM IT MAY CONCERN:

Be it known that we, Jae Chang JUNG, a citizen of the Republic of Korea, residing at #107-1304 Hyundai Apt., Sadong-ri, Daewol-myeon, Ichon-shi, Kyoungki-do 467-850, Republic of Korea, and Geun Su LEE, a citizen of the Republic of Korea, residing at #103-302 Samick Apt., Bubal-eub, Shinha-ri, Ichon-shi, Kyoungki-do 467-860, Republic of Korea, and Ki Soo SHIN, a citizen of the Republic of Korea, residing at #307-1301 Kisan Apt., Yatop-2-dong, Bundang-gu, Sungnam-shi, Kyoungki-do 463-070, Republic of Korea, have invented a new and useful CHEMICAL AMPLIFICATION PHOTORESIST MONOMERS, POLYMERS THEREFROM AND PHOTORESIST COMPOSITIONS CONTAINING THE SAME, of which the following is a specification.

**CHEMICAL AMPLIFICATION PHOTORESIST  
MONOMERS, POLYMERS THEREFROM AND  
PHOTORESIST COMPOSITIONS CONTAINING THE SAME**

5    Technical Field

Novel photoresist monomers, polymers thereof, and photoresist compositions using the same are disclosed. In particular, chemical amplification photoresist polymers and photoresist compositions are disclosed which are suitable for a photolithography process using a light source such as VUV (157 nm) in 10 fabricating a minute circuit for a highly integrated semiconductor device.

Background

In general, a useful photoresist for ArF or VUV (vacuum ultraviolet) should have low absorbency at 193 nm and 157 nm wavelengths, excellent etching 15 resistance and adhesiveness on the substrate, and should be able to be developed in a commercially available developing solution, such as 2.38 wt% and 2.6 wt% aqueous tetramethylammonium hydroxide (hereinafter abbreviated to as “TMAH”) solution.

Recently, much research has been conducted on resins having a high transparency at a wavelength of 248 nm and 193 nm and dry etching resistance 20 similar to novolac resin. However, most of these photoresists cannot be deposited in a sufficient thickness to render a suitable dry etching resistance. Also, these recently developed resins have poor transmittance at 157 nm wavelength.

A photoresist for 157 nm should have excellent etching resistance, heating resistance and adhesiveness on the substrate, and should be able to be developed in 2.38 25 wt% aqueous TMAH solution as a conventional developing solution. However, it is very difficult to synthesize such a polymer that satisfies all these requirements.

For use of a light source of a short wavelength (157 nm), photosensitive agents are available with transparency for the light source of 157 nm, but the available organic photoresist polymers absorb light having a wavelength of 157 nm.

Thus, the primary problem to be solved first when forming a micro pattern of 100 nm or less by using extremely short wavelength (157 nm) is to develop a photoresist polymer which has excellent etching resistance, heat resistance, adhesive property and good transmittance at 157 nm wavelength, and which can be developed in conventional 2.38 wt% aqueous TMAH developing solution.

Therefore, there is a need for a photoresist composition that overcomes the above-mentioned disadvantages.

### **SUMMARY OF THE DISCLOSURE**

Chemical amplification photoresist monomers containing imide and fluorine which has appropriate transmittance of a light source of 157 nm in a photolithography process are disclosed.

Photoresist polymers containing the above photoresist monomers and which has appropriate transmittance of a light source of 157 nm in a photolithography process are also disclosed.

Photoresist compositions containing the photoresist polymers described above and a process for forming a photoresist pattern using the photoresist composition are also disclosed.

Semiconductor elements produced using the photoresist composition described above are also disclosed.

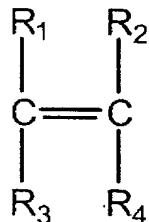
### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure. 1 is a photograph showing a pattern obtained in Example 4.

**DETAILED DESCRIPTION OF THE  
PRESENTLY PREFERRED EMBODIMENTS**

A chemical amplification photoresist monomer is disclosed that contains a halogen structure, that is represented by following Chemical Formula 1, and that is characterized by a strong etching resistance.

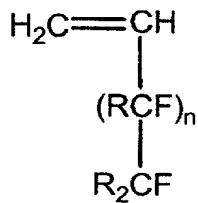
Chemical Formula 1



wherein,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  individually represent a hydrogen or a halogen-substituted alkyl; and wherein that at least one of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is a halogen-substituted alkyl.

The monomer can be preferably represented by following Chemical Formula 2:

Chemical Formula 2



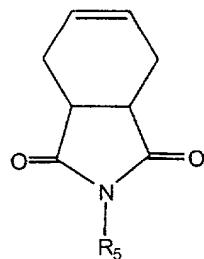
wherein,  $R$  is H or F; and  $n$  is an integer from 1 to 5.

As a preferable example of the monomer represented by Chemical Formula 2 is 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene.

A photoresist copolymer can comprise the monomer represented by Chemical Formula 1.

The copolymer may further comprise the compound represented by following Chemical Formula 3, which has a function of inhibiting dissolution.

Chemical Formula 3



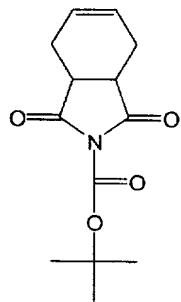
wherein, R<sub>5</sub> is COOR'; and R' is an acid labile protecting group.

The acid labile protecting group is the one that can be released by acid, which prevent the compound from dissolving in an alkaline developing solution.

Some of conventional acid labile protecting group is bounded to polymer, the dissolution of photoresist material by alkaline developing solution is inhibited, while, if the acid labile protecting group is released by acid generated by light exposure, the photoresist material can be dissolved in developing solution. As the acid labile protective group, any groups that can serve such a role may be used; the groups include what are disclosed in US 5,212,043 (May 18, 1993), WO 97/33198 (September 12, 1997), WO 96/37526 (November 28, 1996), EP 0 794 458 (September 10, 1997), EP 0 789 278 (August 13, 1997), US 5,750,680 (May 12, 1998), US 6,051,678 (April 18, 2000), GB 2,345,286 A (July 5, 2000), US 6,132,926 (October 17, 2000), US 6,143,463 (November 7, 2000), US 6,150,069 (November 21, 2000), US 6,225,020 B1 (May 1, 2001), US 6,235,448 B1 (May 22, 2001) and US 6,235,447 B1 (May 22, 2001). Preferred acid labile protecting groups are selected from the group consisting of t-butyl, tetrahydropyran-2-yl, 2-methyl tetrahydropyran-2-yl, tetrahydrofuran-2-yl, 2-methyl tetrahydrofuran-2-yl, 1-methoxypropyl, 1-methoxy-1-methylethyl, 1-ethoxypropyl, 1-ethoxy-1-methylethyl, 1-methoxyethyl, 1-ethoxyethyl, t-butoxyethyl, 1-isobutoxyethyl and 2-acetylmenth-1-yl.

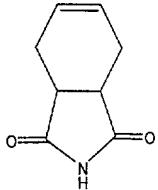
Preferably, the compound of Chemical Formula 3 includes N-(alkyloxycarbonyl)cis-4-cyclohexene-1,2-dicarboxylic imide, especially, N-(tert-butyloxycarbonyl)cis-4-cyclohexene-1,2-dicarboxylic imide of following Chemical Formula 3a.

Chemical Formula 3a



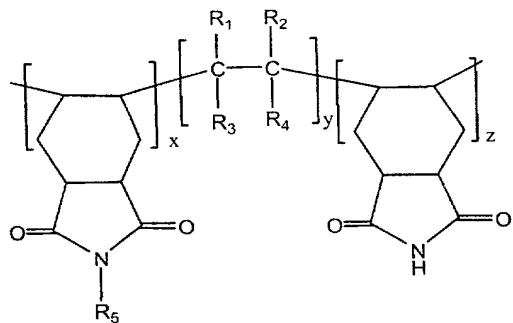
In addition, the copolymer according to the present invention contains the cis-4-cyclohexene-1,2-dicarboxyimide of following Chemical Formula 4.

Chemical Formula 4



A preferred photoresist copolymer has repeating unit represented by following Chemical Formula 5. The polymerization repeating unit of Chemical Formula 5 has high etching resistance due to the cyclic ring back bone, and the monomer component contains fluorine, to provide excellent transmittance and etching resistance for VUV (157 nm).

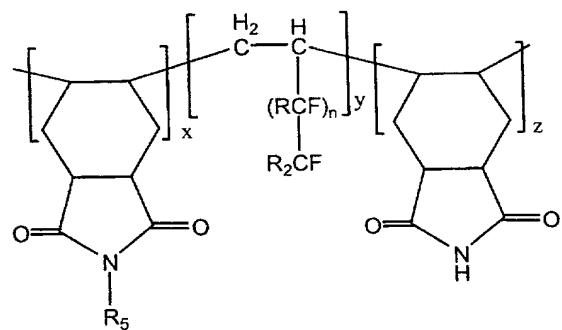
Chemical Formula 5



wherein,  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  individually represent a hydrogen or a halogen-substituted alkyl; and wherein at least one of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is a halogen-substituted alkyl;  $R_5$  is  $COOR'$ ;  $R'$  is an acid labile protecting group; the mol% ratio  $x : y : z$  falls within the ranges 0 to about 40 mol% : 20 to about 40 mol% : 0 to about 50 mol%; preferably, 20 to about 40 mol% : 20 to about 40 mol% : 20 to about 50 mol%; and more preferably, about 30 mol% : about 30 mol% : about 40 mol%.

Preferable example of the polymerization repeating unit can be represented by the following Chemical Formula 6:

Chemical Formula 6



wherein,  $R$  is H or F;  $R_5$  is  $COOR'$ ;  $R'$  is an acid labile protecting group;  $n$  is an integer from 1 to 5; the mol% ratio  $x : y : z$  falls within the ranges 0 to about 40 mol% : 20 to about 40 mol% : 0 to about 50 mol%; preferably, 20 to about 40 mol% :

20 to about 40 mol% : 20 to about 50 mol%; and more preferably, about 30 mol% : about 30 mol% : about 40 mol%.

In addition, the photoresist composition comprising the repeating unit of Chemical Formula 6 exhibits low absorbance at 157 nm wavelength range, and excellent etching property.

The disclosed polymers can be prepared by various methods.

In one particularly preferred method, polymers are prepared by the process including the steps of:

- (a) admixing (i) compound of Chemical Formula 1, optionally (ii) at least of the compounds of Chemical Formula 3 and Chemical Formula 4; and
- (b) adding a radical polymerization initiator or metal catalyst into the resultant to perform a polymerization.

The polymerization processes include the processes disclosed by US 5,212,043 (May 18, 1993), WO 97/33198 (September 12, 1997), WO 96/37526 (November 28, 1996), EP 0 794 458 (September 10, 1997), EP 0 789 278 (August 13, 1997), US 5,750,680 (May 12, 1998), US 6,051,678 (April 18, 2000), GB 2,345,286 A (July 5, 2000), US 6,132,926 (October 17, 2000), US 6,143,463 (November 7, 2000), US 6,150,069 (November 21, 2000), US 6,225,020 B1 (May 1, 2001), US 6,235,448 B1 (May 22, 2001) and US 6,235,447 B1 (May 22, 2001). The step (a) is preferably carried out in a conventional organic solvent, for example, tetrahydrofuran, chlorobenzene, cyclohexanone, cyclopentanone, dimethylformamide, dimethylsulfoxide, dioxane, benzene, toluene, xylene, propylene glycol methyl ether acetate and mixtures thereof.

The polymerization initiators can be any conventional one, preferably radical polymerization initiator, for example, 2,2'-azobisisobutyronitrile(AIBN), benzoylperoxide, acetylperoxide, laurylperoxide or tert-butylperoxide.

In case of using metal catalyst, single or mixed catalyst selected from the group consisting of palladium ethylhexanoate, palladium (II) bis(trifluoroacetate), palladium (II) bis(acetylacetone), palladium (II) 2-ethylhexanoate, palladium (II) bromide, palladium (II) chloride, palladium (II) iodide, monoacetonitriletris(triphenylphosphine)palladium (II) tetrafluoroborate, tetrakis(acetonitrile)palladium (II) tetrafluoroborate, dichlorobis(acetonitrile)palladium (II), dichlorobis(triphenylphosphine)palladium (II), dichloro(benzonitrile)palladium (II), palladium acetylacetone, palladium bis(acetonitrile)dichloride, palladium bis(dimethylsulfoxide)dichloride, nickel ethylhexanoate, nickel carboxylate, nickel diketylglyoxime, nickel ethylacetyl hexanoate and bis(allyl)nickel, is preferably used.

More preferably, after polymerization the polymer is subject to crystallization and/or purification by using a suitable solvent, for example, diethyl ether, petroleum ether, hexane, alcohols (methanol, ethanol, isopropanol, or the like), water, or mixtures thereof.

In addition, the present invention provides a photoresist composition containing (i) a photoresist polymer described above; (ii) a photoacid generator; and (iii) an organic solvent.

As of photoacid generator, which is able to generate acid when it is exposed to light, and as organic solvent, conventional ones may be employed. The processes for preparing the composition include what is disclosed by US 5,212,043 (May 18, 1993), WO 97/33198 (September 12, 1997), WO 96/37526 (November 28, 1996), EP 0 794 458 (September 10, 1997), EP 0 789 278 (August 13, 1997), US 5,750,680 (May 12, 1998), US 6,051,678 (April 18, 2000), GB 2,345,286 A (July 5, 2000), US 6,132,926 (October 17, 2000), US 6,143,463 (November 7, 2000), US 6,150,069 (November 21, 2000), US 6,180,316 B1 (January 30, 2001), US 6,225,020

B1 (May 1, 2001), US 6,235,448 B1 (May 22, 2001) and US 6,235,447 B1 (May 22, 2001).

Preferred photoacid generators include sulfide or onium type compound. Specifically, photoacid generator is selected from the group consisting of phthalimidotrifluoromethanesulfonate, dinitrobenzyl tosylate, n-decyldisulfone and naphthylimidotrifluoromethanesulfonate, which has relatively low absorbance at 157 nm and 193 nm. Together with the compounds, a photoacid generator selected from the group consisting of diphenyliodide hexafluorophosphate, diphenyliodide hexafluoroarsenate, diphenyliodide hexafluoroantimonate, diphenyl-p-methoxyphenyl triflate, diphenyl-p-toluenyl triflate, diphenyl-p-isobutylphenyl triflate, triphenylsulfonium hexafluoroarsenate, triphenylsulfonium hexafluoroantimonate, triphenylsulfonium triflate and dibutylnaphthylsulfonium triflate may be used.

The photoacid generator is preferably used in an amount of 0.05 to 10 wt% of the photoresist polymer. If the amount is less than 0.05 wt%, sensitivity of the photoresist to light becomes insufficient, while if it is more than 10 wt%, the photoacid generator largely absorbs far ultraviolet to generate too much acid to deteriorate the cross section of the pattern.

As the organic solvent, any organic solvent conventionally used for the photoresist composition can be used; single or mixed solvent of diethyleneglycol diethyl ether, ethyl 3-ethoxypropionate, methyl 3-methoxy propionate, cyclohexanone, propyleneglycol methyl ether acetate, n-heptanone, ethyl lactate or cyclopentanone is preferably used.

The amount of solvent used is preferably in the range of from about 500 to 2000 wt% of the photoresist polymer. This ratio has been found to be particularly useful for obtaining a photoresist layer of a desirable thickness when coated on to a substrate.

In addition the present invention provides a process for forming a photoresist pattern, comprise the steps of:

- (a) coating the photoresist composition described above on a substrate to form a photoresist film;
- (b) exposing the photoresist film to light; and
- (c) developing the photoresist film.

The process for forming the photoresist pattern can further include a soft baking step which is performed before the step (b) and/or a post baking step which is performed after the step (b). Preferably, the soft and post baking steps are performed at the temperature of from about 70 to about 200°C.

Exemplary light source which are useful for forming the photoresist pattern include KrF, ArF, E-beam, VUV, EUV or ion beam. Preferably, the irradiation energy in the step (b) is in the range of between about 1mJ/cm<sup>2</sup> and about 100 mJ/cm<sup>2</sup>.

The disclosed monomers, polymers and photoresist compositions will now be described in more detail by referring to the examples below, which are not intended to be limiting.

#### I. Preparation of catalyst solution

##### Example 1--Preparation of catalyst solution

Under nitrogen atmosphere, allylpalladium chloride dimer (allyl<sub>3</sub>PdCl<sub>2</sub>)<sub>2</sub> (176.4 mg) and silver hexafluoroantimonate (AgSbF<sub>6</sub>) (510 mg) were added to 30 ml of chlorobenzene, and the mixture was heated under reflux for about 30 minutes to prepare the catalyst solution.

#### II. Preparation of photoresist polymer

##### Example 2--Synthesis of

poly(N-(tert-butyloxycarbonyl)cis-4-cyclohexene-1,2-dicarboxylic imide / 3,3,4,4,5,5,6,6,6- nonafluoro-1-hexene / cis-4-cyclohexene-1,2-dicarboxyimide

N-(tert-butyloxycarbonyl)cis-4-cyclohexene-1,2-dicarboxylic imide (1.5 g) of Chemical Formula 3a, 3,3,4,4,5,5,6,6,6-nonafluoro-1-hexene (2 g) and cis-4-cyclohexene-1,2-dicarboxyimide (1.5 g) were dissolved in 45 ml of chlorobenzene, and the mixture was heated under reflux for 30 minutes. After heating under reflux, the catalyst solution obtained from Example 1 after it was passed through a syringe filter of 0.4  $\mu$ m to remove impurities, was added to the reaction mixture, and the resultant mixture was reacted at room temperature for 48 hours. After the reaction was completed, polymer precipitate was taken from ethyl ether and dried in vacuo to obtain title compound (yield: 51%).

Weight average molecular weight of the polymer was 15,000, and polydispersibility (weight average molecular weight / number average molecular weight) was 1.6.

### III. Preparation of photoresist composition and pattern formation

#### Example 3--Transmittance against 157 nm

The photoresist polymer (1 g) prepared from Example 2 was dissolved in cyclohexanone (10 ml), and transmittance against 157 nm was measured. At the film thickness of 0.2  $\mu$ m, optical density was 0.6, and it was useful for a photosensitive agent at 157 nm.

#### Example 4--Preparation of photoresist composition and formation of micro pattern

Photoresist polymer prepared from Example 2 (1 g) and triphenylsulfoniumtriflate (0.02 g) as photoacid generator were dissolved in 10 ml of cyclohexanone, and the solution was heated under reflux for 2 hours to prepare photoresist composition.

The photoresist composition was coated on a silicon wafer that had been treated with hexamethyldisilazane (HMDS), and baked at 130°C for 90 seconds. After baking, it was light exposed by using a light exposing device employing

light source for 193 nm wavelength, and baked again at 130°C for 90 seconds. Then, the composition was developed in 2.38 wt% TMAH solution for 90 seconds to give 0.15  $\mu$ m L/S pattern (see Fig. 1).

As seen from Example 3, the photoresist polymer according to the present invention has excellent transmittance at 157 nm wavelength, so that it can be useful for photolithography process using a light source of 157 nm. Further, it is found, from Example 4, that the photoresist composition according to the present invention can be adopted to conventional lithography process.

A chemical amplification photoresist polymer containing imide and fluorine and a photoresist composition comprising the polymer can be employed in lithography process using VUV (157 nm) light source.